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 $\text{Pd}(46)$ $\text{Rh}(45)$ AND $\text{Ru}(44)$

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN.

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GEORGE D. VAN DYKE

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ABSTRACT

The *L* x-ray absorption edges of the elements Sn (50), In (49), Cd (48), Ag (47), Pd (46), Rh (45) and Ru (44) have been photographed and measured with a Siegbahn vacuum spectrograph of the precision type. The absorbing screens were made of the pure elements, since in this case the values of the energy levels obtained are admittedly more characteristic of the element than if chemical compounds were used as absorbers. Tables of wave-lengths of absorption edges and associated energy levels are given.

THE purpose of this investigation was to photograph and measure the *L* absorption limits of the elements immediately below Sb (51) in the periodic table. Most of these limits had previously been only calculated either by extrapolation from the values for adjacent elements in the periodic table, or by combining the values for the *K* edge with those of emission lines. The latter process gave somewhat unreliable values on account of the fact that a small error in λ for a *K* edge or line corresponds to a comparatively large error in ν for the *L* edge.

It has been known for some time that the position of the absorption edge depends upon the chemical combination of the element in a compound, and that the principal edge is usually accompanied by a series of absorption "lines" or fine structure on the short wave-length side. In view of this fact it was thought an investigation with the pure elements would give energy values more characteristic of the substance.

A Siegbahn vacuum spectrograph of the precision type was used with a crystal-plate distance of 178.82 mm. The electron tube was evacuated by a double stage mercury diffusion pump described by Kurth.¹ This pump was backed by a double-stage General Electric oil pump which alone evacuated the camera. The high tension was supplied by a Thordarson 2.5 k.w., 25,000 v transformer. The tube was self-rectifying. The filament was a spiral of tungsten wire about ten mils in diameter which was wound on a special form designed for the purpose. Molybdenum and copper anodes were used, while a calcite crystal, ground and polished by hand, reflected the rays. The x-ray plates used were made by the Eastman Kodak Company. The edges were measured on a Gaertner comparator reading to 0.001 mm.

On account of the comparatively long wave-lengths in the region investigated one of the greatest difficulties encountered was to secure absorbing screens of the proper thickness. The absorption of an element for its own characteristic radiation varies approximately as the inverse square of the atomic number. For the lighter elements, therefore, the screens must be

¹ Kurth, Science 54, p. 608 (1921).

very thin to allow any appreciable radiation to get through. Again, as one goes lower in the periodic table, there seems to be little doubt that the process which gives rise to the critical absorption is less marked, it being difficult or impossible, in some cases, to locate the edges even when the blackening on the plate indicates that considerable radiation has been transmitted by the screen. The L_I edge of ruthenium could not be located satisfactorily although a large number of plates were carefully examined.

The screens for most of the elements used were thin sheets rolled in a rolling machine. Tin, cadmium, and indium are very malleable. With suitable care, cadmium and tin may be rolled to practically any thickness desired. Indium, being especially malleable and soft, presented unusual difficulties. Although it rolls into very thin sheets these can only with great difficulty be taken from the rollers without tearing them and thus rendering them unfit for absorbing screens. Finally the indium was rolled between two sheets of rough paper. Since ordinary paper is fairly transparent to wave-lengths in this region, very satisfactory screens were made in this manner. Palladium is a much harder metal than any of the three mentioned above and although it rolls out into thin sheets these are in most cases not at all uniform, but present to the eye a sieve-like appearance. Although a uniformly thin film would undoubtedly give a better edge, it was found that this uniformity was not at all necessary. Rhodium and ruthenium were secured in powdered form. They were pulverized as finely as possible by grinding in a mortar and then thoroughly mixed in collodion. This mixture was then poured out on a glass plate and allowed to dry. By tipping the plate and allowing the mixture to spread, films of varying thickness were easily secured. Screens of silver were rolled similar to those of the other metals. These gave excellent L_{III} and L_{II} edges. If one assumes that the chemical action of the light on the plate depends upon the absorption of light by, and consequent reduction of, the Ag^+ it is rather surprising to find intense blackening on the long wave-length side of the edge, this being a very transparent region for the Ag film of the plate. The metal screens varied in thickness from approximately 0.004 to 0.01 m m.

Although no quantitative measurements were taken, it appeared very probable that there exists an optimum thickness of the screen for each of the L edges individually. Screens which gave good L_I edges were in most cases not satisfactory for L_{II} and L_{III} . This is not at all conclusive, as there are so many variable factors entering in which make it difficult to separate the individual effects. Among these are: the time of exposure, the voltage, the tube current, and the sharpness of the focus of the cathode stream on the anode surface.

The general law of absorption of x-rays is expressed in the form $I = I_0 e^{-\mu x}$ where I_0 is the incident intensity and I is the intensity of the beam after having traversed a thickness x of the absorbing material. If the absorption coefficient μ is different on the two sides of an absorption edge we may write $I_1 = I_0 e^{-\mu_1 x}$ for the transmitted intensity just above the edge and $I_2 = I_0 e^{-\mu_2 x}$ for the corresponding intensity immediately below the edge. For the greatest

contrast on the photographic plate $I_1 - I_2$ should be a maximum, i.e., $d(I_1 - I_2) = 0$. This corresponds to a thickness $x = (\log \mu_2 - \log \mu_1) / (\mu_2 - \mu_1)$. As no data on the values of the absorption coefficients were available at the time of this investigation no systematic attempt was made to secure screens of this optimum thickness. Since, Allen² has published values of the mass absorption coefficients for two of the elements used, viz., Ag and Sn, which make possible a rather interesting calculation. From Allen's data it is not possible to take values on opposite sides of the three L edges individually. However, by using his value of $\mu/\rho = 980$ for Sn for a wave-length of 2.60Å which lies just below the L_I limit, and 390 for a wave-length of 3.22Å just above the L_{III} limit for the same element, we arrive at a thickness of 0.0021 mm for maximum contrast between these two points on the photographic plate. A similar calculation for Ag gives a value of 0.0011 mm. These values might be regarded as giving the right order of thickness for satisfactory absorbing screens for obtaining the L limits of these elements. To roll screens of this thickness would require a great deal of skill and care.

All measurements on the edges were made with respect to standard emission lines using wave-lengths given in Siegbahn's "Spectroscopy of X-Rays." The lines from the copper anode and those from the tungsten which evaporated from the tungsten filament on to the anode, often fell in convenient places for reference. In other cases suitable lines were secured by rubbing different materials on the anode. Often it was necessary to keep the voltage low to prevent emission lines of higher orders from obscuring the edges and in most cases it seemed advisable to keep the voltage so low that no appreciable amount of second order general radiation fell on the plate.

In common with lines in this region most of the edges were diffuse. This no doubt was due in part to the rather wide slit width of 0.1 mm. L_{III} of tin showed the sharpest discontinuity. The presence of the edges was unmistakable, however, and all with the exception of L_I of palladium were measured on the comparator. The L_I edges were measured with the least certainty. The maximum error, certainly not more than 0.1 mm, in locating it, occurred with palladium where an error of this magnitude corresponds to 1.3 X.U. and to 0.1 unit in ν/R .

The time of exposure varied from 2.5 hours for the strong L_{III} to as much as 8 hours for the weaker L_{II} and L_I edges. The average length of exposure was about 4 hours with a tube current of 20 milliamperes. In all the calculations, the value of d , the grating constant for calcite, was taken as 3029.04 X.U. which is the accepted value for the spectrum of the first order from calcite. The values of the wave-lengths in x-units are given in Table I. These represent the averages from at least three plates in every case and in some cases as many as seven. Corresponding values of ν/R and of $(\nu/R)^{1/2}$ will also be found in Table I. The values of $(\nu/R)^{1/2}$ are plotted against atomic number in Fig. 1. Considering the large scale used, the points lie remarkably close to the straight lines. The constancy of $\Delta(\nu/R)^{1/2}$ for the

² Allen, Phys. Rev. 28, p. 907 (1926).

TABLE I

Values of the wave-length, of ν/R , and of $(\nu/R)^{1/2}$ for the L absorption limits of certain elements.

	Wave-length (X. U.)			ν/R			$(\nu/R)^{1/2}$		
	L_I	L_{II}	L_{III}	L_I	L_{II}	L_{III}	L_I	L_{II}	L_{III}
44Ru		4169.3	4360.4		218.57	208.99		14.78	14.16
45Rh	3618.6	3934.0	4121.2	251.83	231.64	221.12	15.87	15.22	14.87
46Pd	3420.6	3715.2	3900.5	266.41	245.28	233.63	16.32	15.66	15.28
47Ag	3247.4	3506.7	3690.8	280.62	259.87	246.94	16.76	16.09	15.71
48Cd	3077.3	3319.2	3496.3	296.13	274.55	260.64	17.21	16.57	16.15
49In	2919.4	3139.5	3315.5	312.14	290.26	274.85	17.67	17.04	16.58
50Sn	2769.6	2972.3	3149.3	329.03	306.59	289.36	18.14	17.51	17.01

screening doublet (L_I - L_{II}) in the region investigated is very evident. Here $\Delta(\nu/R)$ for the screening doublet is larger than that for the "relativity" doublet, (L_{II} - L_{III}). At barium this situation is reversed, for elements higher than barium in the periodic table, $\Delta(\nu/R)$ for the "relativity" doublet is

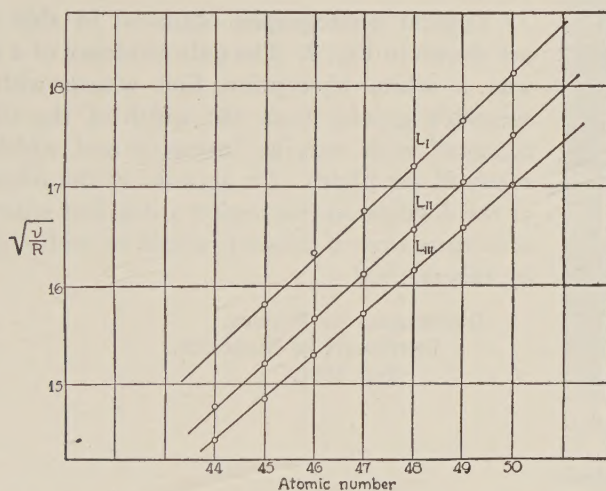


Fig. 1. Plot of the values of $(\nu/R)^{1/2}$ for the L_I , L_{II} and L_{III} absorption limits as a function of atomic number.

the greater. Energy level values for the elements investigated based upon the values obtained in this investigation are given in Table II. The values given in parentheses are regarded as of little significance, being well within the experimental error involved in these measurements.

TABLE II

Energy level values (ν/R)

	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	$N_{III,IV}$	N_V	O_I
44 Ru	—	218.6	209.0	42.7	—	—	20.9	20.5	5.6	—	—	.2	(.08)
45 Rh	251.8	231.6	221.1	45.6	38.8	37.1	22.8	22.5	5.8	4.3	.1	(.03)	
46 Pd	266.4	245.3	233.6	49.2	42.1	40.0	25.0	24.5	6.2	4.6	.1	(.02)	
47 Ag	280.6	259.9	246.9	53.1	44.6	42.3	27.6	27.1	6.8	4.4	.6	.2	
48 Cd	296.1	274.6	260.6	56.9	48.1	45.5	30.3	29.8	8.0	4.9	.8	.7	
49 In	312.1	290.3	274.8	61.0	51.7	48.9	33.4	32.7	9.1	5.7	1.5	1.2	(.0)
50 Sn	329.0	306.6	289.4	65.4	55.9	52.8	36.6	35.7	10.1	7.0	2.3	1.7	.2

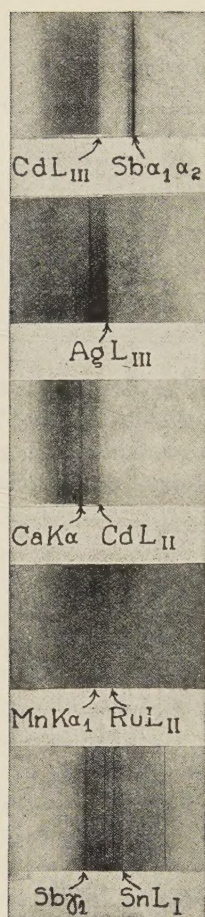


Fig. 2. Typical photographs of the L absorption edges.

Since the completion of this work Coster and Mulder³ have reported values for the L edges of all the elements here listed with the exception of L_{II} and L_{III} of tin and L_{II} of palladium. In some instances their absorbing screens were of the pure metal, but in a majority of cases the elements occurred in various compounds. There seems to be no systematic variation between their values and ours. Mulder used a gypsum crystal with a crystal-plate distance of 13.03 cm. Because of this smaller dispersion it is reasonable to suppose that the accuracy with the gypsum crystal in locating the edge should be somewhat less than with calcite. In view of this fact it is safe to assume that the values agree within the experimental error, with the possible exception of the L_{II} edge of indium, the difference here being approximately 11 X.U.

Typical photographs obtained in this investigation are shown in Fig. 2. The only evidence of a fine structure was a white absorption line whose width was considerably greater than the width of the slit. This line occurred with varying intensity and width on a great many of the plates. On account of the relative faintness of the L edges in this region a detailed study of any fine structure, even if present, would be well-nigh impossible by this method.

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UNIVERSITY OF MICHIGAN,
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³ Mulder, Doctor's Dissertation, Groningen, 1927.



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